



INSTITUTE OF
ENERGY CONVERSION

University of Delaware
Newark, DE 19716-3820
Ph: 302/831-6200
Fax: 302/831-6226
www.udel.edu/iec

UNITED STATES DEPARTMENT OF ENERGY
UNIVERSITY CENTER OF EXCELLENCE
FOR PHOTOVOLTAIC RESEARCH AND EDUCATION

February 01, 2005

Ken Zweibel
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, CO 80401

Re: NREL Subcontract #ADJ-1-30630-12

Dear Ken:

This report covers research conducted at the Institute of Energy Conversion (IEC) for the period from Dec. 04, 2004 to Jan. 03, 2005, under the subject subcontract. The report highlights progress and results obtained under Task 1 (CdTe-based solar cells).

TASK 1 – CdTe-BASED SOLAR CELLS

CdTe surface chemistry

Understanding aniline etching of CdTe

Experiments to confirm the mechanism of CdTe etching in aqueous aniline-based solutions under illumination has continued. To understand the nature of aniline during treatment, it was replaced with aniline hydrochloride, which consists of the protonated, or conjugate acid, form of aniline ($\text{C}_6\text{H}_5\text{-NH}_3^+$) balanced with a Cl^- anion. The action of a bath based on this species will indicate the active form of aniline during treatment.

Treatment of vapor transport deposited CdTe, without CdCl_2 annealing, was carried out in aqueous baths containing 0.1M aniline hydrochloride, 0.01M p-toluenesulfonic acid and 1M NaCl or in aqueous baths of just 0.1M aniline hydrochloride. The pH of these baths was ~ 1.9 , significantly more acidic than the standard aniline-based baths of pH ~ 6 . Treatments were carried out for 90 min either under illumination or in the dark. All treatments, irrespective of illumination, produced identical results of only very minor etching of the CdTe surface, significantly less than that observed for CdTe treatment in standard aniline baths under illumination. This result does indicate that the deprotonated form of aniline ($\text{C}_6\text{H}_5\text{-NH}_2$) is the active agent in the treatment. HCl present in the bath likely causes the minor etching of the

CdTe surface. These results are consistent with past observations for baths where the concentration of p-toluenesulfonic acid was increased, but which showed no reaction with CdTe. Both of these observations are consistent with the chemistry of aniline, where the protonated form has been shown to be more difficult to oxidize and, therefore, will be less reactive towards CdTe. Bath pH must be carefully controlled to assist aniline solubility, but without producing significant concentrations of the protonated species.

The high toxicity of aniline remains a significant factor when considering any possible applications of this treatment. It is prudent to explore possible safer alternatives to replace aniline. Successful alternates require a number of criteria to be met, including; low toxicity, safe and easy handling, be reasonably soluble in water, have an oxidation potential similar to aniline, and oxidation products must be non-reactive towards CdTe and Te. Aniline is a successful etchant of CdTe as its oxidation results in the formation of unreactive polyaniline. In our previous report, the use of potassium ferrocyanide, $K_4Fe(CN)_6$, as a possible aniline substitute was described. This species met most of the above criteria and baths etched CdTe with illumination. However, the product of oxidation, $Fe(CN)_6^{3-}(aq)$, reacts with CdTe and Te, forming surface oxides of Te and Cd, which are deleterious to back contact formation. We have explored some possible aniline substitutes, including ascorbic and citric acids, catechol (1,2-dihydroxybenzene) and methanol. Illuminated treatments with baths containing these species showed no action on the CdTe surface. These species, however, did not necessarily meet each of the above criteria, but did assist understanding of the requirements for successful bath chemistry. The search for a safer alternative reagent continues.

High Throughput Processing

Effect of CdTe thickness

The vapor transport (VT) deposition system has been used to investigate a wide range of CdTe deposition rates and reduced film thickness. Baseline deposition conditions were established to provide benchmark values for comparison:

Source temperature = 800°C

Substrate temperature = 550°C

Carrier gas flow rate = 20 sccm

Operating pressure = 20 Torr

Oxygen partial pressure = 0.05 Torr

Translation speed = 2.5 cm/min

These conditions yield a deposition rate of $\sim 10 \mu\text{m}/\text{min}$ and film thickness of 5-6 μm . The growth rate was varied from 6 $\mu\text{m}/\text{min}$ to $>80 \mu\text{m}/\text{min}$ by increasing source temperature and carrier gas flow rate. The substrate translation speed was adjusted accordingly to maintain film thickness of $\sim 5 \mu\text{m}$. Similarly, fixing the source conditions and increasing the translation speed to 12 cm/min obtained CdTe films with thickness of 1 mm. The deposition conditions have a significant effect on the CdTe film morphology, in accordance with the general principles of vapor deposition: grain size increases with film thickness and substrate temperature and decreases with increasing growth rate. Grain size in PVD, VT and electrodeposited (ED) CdTe

is a valuable metric for deciding the conditions of the CdCl_2 treatment, since CdS consumption via diffusion during CdCl_2 treatment increases with decreasing grain size. Obtaining moderate conversion efficiency in 1-2 μm thick PVD and ED films required performing the CdCl_2 vapor treatment at temperatures in the range from 380°C to 390°C, which is 20-30°C lower than needed for 3-5 μm thick films. Figure 1 shows the thickness dependence of grain size for CdTe films deposited at the same source conditions but at different translation speeds, resulting in 5 mm and 1 μm thickness, at 550°C substrate temperature.

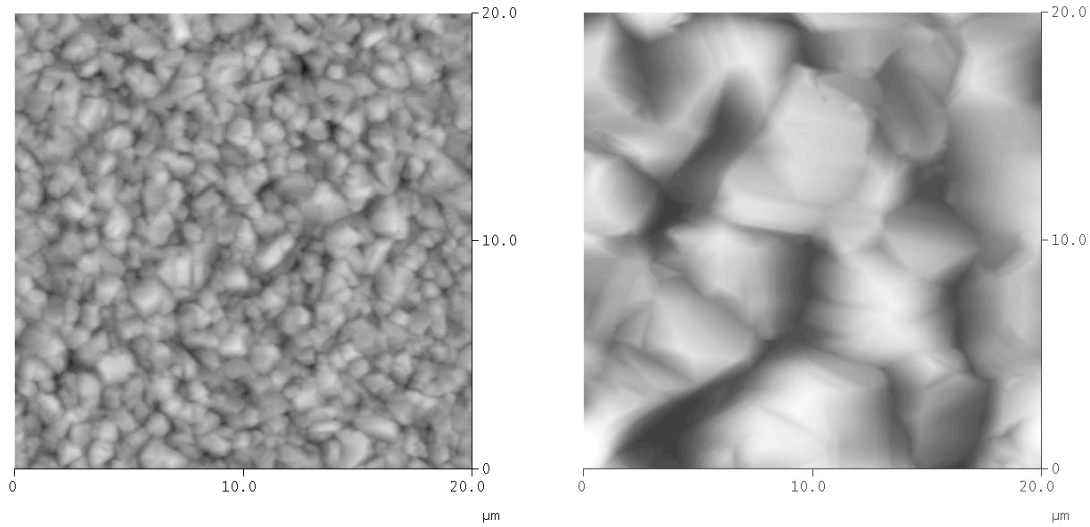


Figure 1. AFM images of 1 μm (left) and 5 μm thick (right) CdTe films deposited by vapor transport on moving substrates in $\text{He}+\text{O}_2$ at 550°C.

Baseline devices were fabricated with CdCl_2 vapor treatment at 415°C for 25 min in Ar/O_2 ambient, followed by BDH etch, Cu/metal (Ni, Cr, or Au) contact evaporation (0.4 cm^2 area), and thermal treatment at 180°C, yielding AM1.5 conversion efficiencies from 12-13%.

For processing cells with 1 μm thick CdTe , post-deposition conditions developed for PVD and ED materials were employed, consisting of CdCl_2 treatment at 390°C for 20 min and reduction of the final treatment temperature to 160°C. For PVD cells, this processing protocol yielded $\eta = 9.3\%$ for devices with 1.3 μm CdTe , compared to $\eta = 11.3\%$ for devices with 4 μm CdTe , with the primary difference occurring in FF.¹ For VT cells, the present best cell results, for the samples of Figure 1, are shown in Table 1.

With respect to CdTe thickness, the cell performance differs primarily in V_{OC} and FF, which shows that 1 μm thickness is adequate for current generation. Unlike PVD cells, however, the junction operation is inferior and must be re-optimized. Devices will be analyzed to determine the cause of reduced performance and process optimization to recover performance.

Table 1. Best-cell J-V results for VT cells with Ni contacts and different CdTe thickness and window layers.

Run	CdTe Thickness (μm)	Window Layer	V _{OC} (mV)	J _{SC} mA/cm ²	FF (%)	η (%)
VT134	6	CdS	804	24.1	62.7	12.1
VT137	6	CdZnS	686	25.3	50.4	8.7
VT139	1	CdS	649	23.3	54.1	8.2

Junction formation

The buffer layer used in the baseline VT process is 50-60 nm thick Ga₂O₃, made by native oxidation of sputtered Ga. Ga₂O₃ was selected based on its high band gap (~4.8 eV), high transparency in the visible portion of the spectrum, high dielectric constant (~10), and good chemical stability ($\Delta H_f = -260$ kcal/mol). In comparative studies with PVD cells, Ga₂O₃ gave consistently higher cell performance than other oxides investigated: In₂O₃, ZnO, SnO₂. In the previous report under this CdTe task (Nov 2004), comparative cell data was presented for VT cells made with In₂O₃ and Ga₂O₃, with Ga₂O₃ yielding consistently higher performance. To follow-up this work, VT cells were fabricated with no buffer layer on the SnO₂. In this case, the adhesion of the CdTe/CdS was very poor, and films delaminated during the contact etch step. This is consistent with our finding that more conformal morphology of the CSD CdS film is obtained for deposition on In₂O₃ and Ga₂O₃ buffer layers than on the TCO materials. The conformal morphology appears to be required for mechanical robustness for cells with solution-grown CdS films.

The CdS heteropartner continues to yield the highest performance in CdTe cells. Other window layers have been proposed based on their anticipated beneficial effect on junction operation by influencing conduction band alignment with CdTe.² To follow-up our work on PVD devices, VT devices are being fabricated with Cd_{0.9}Zn_{0.1}S window layers deposited by chemical surface deposition from cadmium and zinc sulfate, thiourea and ammonia (Table 1). As with PVD cells, higher J_{SC} was obtained due to improved blue response. However, unlike the PVD results, the junction is significantly poorer, despite the presence of the Ga₂O₃ buffer layer. More detailed device analysis is needed to resolve the different junction operation with different window and buffer layers.

The role of CdTe source purity in affecting CdTe film defects and their role in controlling junction operation is a poorly understood area with potential for producing significant improvement. The VT process, with access to a wide range of deposition temperatures and ease of source replacement, will be used to investigate the effects of substrate temperature and source composition on device operation. CdTe source materials of different purity have been obtained and will be run under baseline deposition and cell fabrication conditions. Witness samples from each deposition and crystals of the raw source material will be analyzed for comparison with

device behavior. As a diagnostic tool, cells with different CdTe thickness, from $< 1 \mu\text{m}$ to $> 10 \mu\text{m}$ will be fabricated to separate primary and contact junction effects.

Device Analysis

Effect of metal contacts on JV performance

Previously, IEC has used either an evaporated Cu followed graphite paste or evaporated Cu/Au for back contacts. In both cases the surface was first prepared to be Te rich to allow formation of the Cu_2Te layer primary contact. However, neither is ideal. The graphite requires additional handling and scribing while the Cu/Au is prone to rapid degradation. So, we investigated evaporated thick Ni, Cr, Au as secondary contacts with and without a 15 nm Cu layer. The Cu and secondary contacts were evaporated sequentially without breaking vacuum. Baseline CdS/CdTe from the VT system was used as substrates. Pieces were annealed at 180°C in Ar for 30 min after metallization. They were $1'' \times 2''$ allowing for 8 cells of 0.36 cm^2 area.

Table 2 lists the JV performance of the best cell and yield for each type of contact. JV curves for the best cell with Ni and Ni/Cu are shown in Figure 2. The V_{OC} is surprisingly high for devices without any Cu in the contact yet they clearly had lower FF, higher R, higher J_0 and the curvature in forward bias indicates a non-ohmic contact. Between the contacts with Cu, Au and Ni gave equivalent performance while Cr lower FF due to higher R. Note that Cr gave lower FF and higher R with or without Cu. The yield was 100% without Cu and 75% with Cu indicating Cu is responsible for the shunting. The efficiency on VT128.6 ranged from 12.5 to 13.6% (average 13.1%) indicating good uniformity.

Table 2. JV performance of best cell with different evaporated metal contacts. Yield is shown for the 8 cells per piece. Dark JV curves were analyzed to obtain R, A and J_0 .

Piece	Contact	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	Eff (%)	Yield	R ($\Omega\text{-cm}^2$)	A	J_0 (mA/cm^2)
VT127.6	Au	0.75	23.5	62	10.9	8/8	10	1.9	$2\text{E-}6$
VT127.5	Cu/Au	0.80	23.0	72	13.2	6/8	1.8	1.7	$5\text{E-}7$
VT128.5	Ni	0.79	23.1	62	11.4	8/8	25	1.9	$2\text{E-}6$
VT128.6	Cu/Ni	0.81	23.7	71	13.6	7/8	2.4	1.6	$1\text{E-}7$
VT128.4	Cr	0.80	22.7	52	9.5	8/8	43	1.7	$9\text{E-}7$
VT128.3	Cu/Cr	0.81	23.0	62	11.7	6/8	4.4	1.7	$2\text{E-}7$

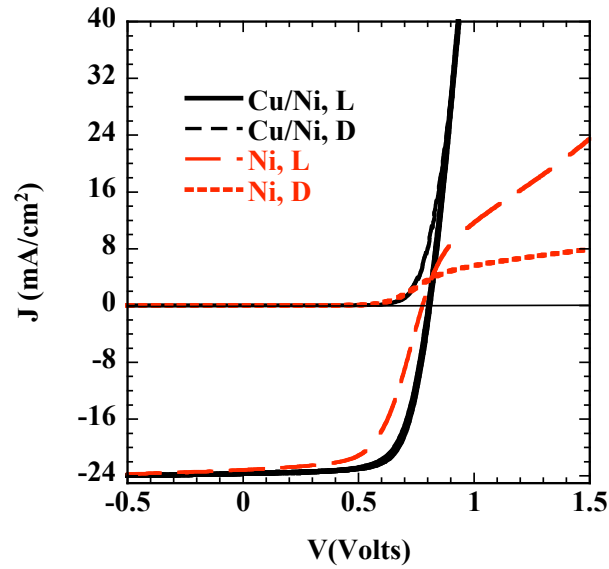


Figure 2. Light and dark JV curves for devices with Cu/Ni (VT128.6) and Ni (VT128.5).

Accelerated stress-testing

Accelerated stressing using the new VT devices was initiated once they had achieved baseline performance of 12-13%. Pieces VT128.5 and 128.6 were selected to investigate the effect of bias voltage during stress on degradation of samples with and without Cu contacts. Previously, it was shown that devices with Cu contact had a stronger bias dependence, degrading more in forward bias than those without Cu contacts.^{3,4} We planned to study whether degradation at open circuit (OC) or far forward bias could be cured by subsequent stress at short circuit (SC) as we had seen previously and as described in Appendix 2 (Hegedus et al presented at the 31st IEEE).

Pieces VT128.5 and 128.6 were stressed at 85°C for 14 days in the light in dry air at various biases. Figure 3 shows V_{OC} vs time for 3 devices from VT128.6 (Cu/Ni) on the same substrate. In contrast, to results reported previously,^{3,4} degradation was very similar between SC or OC, decreasing only 40-60 mV and nearly leveling off after only 4 days. A third cell was at OC for 4 days, then at 1.3xOC (corresponding to the forward bias current of $\sim 2 \times J_{SC}$) for 4 days, resulting in accelerated degradation. When switched to SC, V_{OC} plummeted ~ 80 mV in a few hours but then continued to decrease slowly for 4 days. V_{OC} recovered just as rapidly when switched to OC. This represents nearly opposite bias dependence from hybrid A/IEC devices in Appendix 2. Figure 4 shows V_{OC} vs time with the same bias sequence for VT128.5 without Cu in the contact. It does not show the stronger decrease with a far forward bias of 1.3xOC as seen in Figure 2. This is consistent with past results.^{3,4} Degradation of V_{OC} at SC or OC is comparable to the cell with Cu in Figure 2, about ~ 50 mV. The cell where bias was switched behaves like the cell with Cu in Figure 3 including the rapid decrease and recovery with SC or OC but the magnitude of change is smaller. Thus, the bias dependent behavior cannot be explained solely by Cu ion drift changing with field polarity. Some results shown here are qualitatively different from those

reported before on different devices: the degradation of V_{OC} at SC and OC are comparable and small, and the degradation of V_{OC} with and without Cu in the contact is similar, about 5-10%. Table 3 shows the relative change in cell performance after stress compared to initial values. The cells without Cu degrade less than those with Cu at OC, as we have seen before. The largest change was in FF. This suggests that the VT material is not more stable against forward bias driven degradation related to Cu motion.

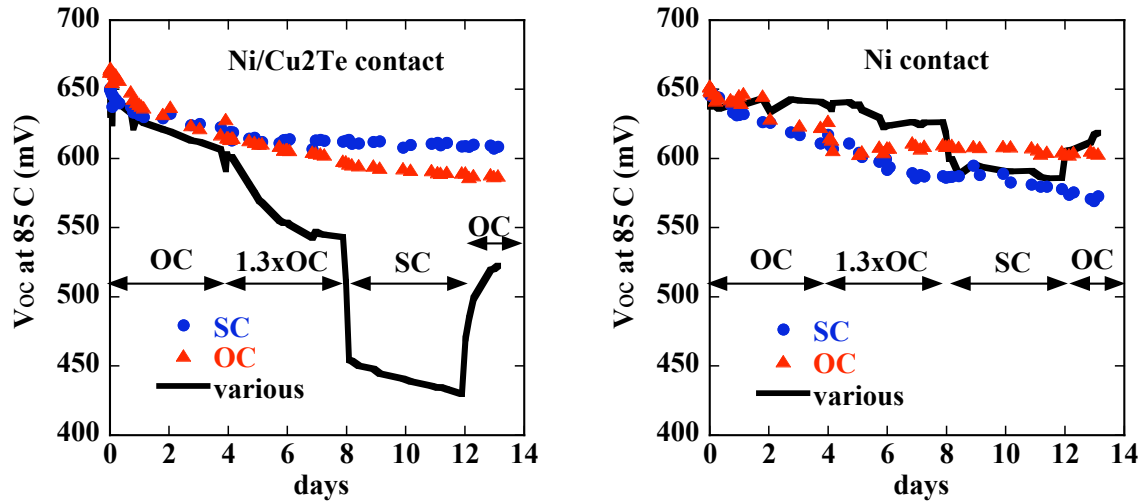


Figure 3 (left) and 4 (right). V_{OC} at 85°C vs time at stress. Cells were at continuous SC or OC bias or switched from OC to 1.3 V_{OC} to SC to OC every 4 days.

Table 3. Relative change in parameters after stress at SC or OC bias for 14 days at 85°C in light.

Piece	Contact	Stress bias	V_{oc} (%)	J_{sc} (%)	FF (%)	Eff (%)
VT128.5	Ni	SC	-7	-2	-11	-19
		OC	-5	-3	-1	-9
VT128.6	Cu/Ni	SC	-5	-2	-13	-19
		OC	-9	-4	-16	-28

Team Activity:

Research was carried out under the materials chemistry and device physics subteams. Oxidation of CdTe films at different humidity levels was investigated by in-situ glancing incidence diffractometry and post-treatment XPS depth profilometry. The development of oxides after deposition, during storage and heating, may influence the defect chemistry and electronic properties of the CdTe film obtained by CdCl₂ and Cu treatment. PVD and VT films were sent to Colorado State University, as part of the team effort, to correlate luminescence signatures in CdTe films with deposition processes and device results. Collaboration with the University of Toledo is underway to investigate the voltage bias dependence of contact adhesion on unstressed and stressed CdTe cells. This work builds on earlier IEC work in which the contact adhesive force on stressed cells (@V_{OC}, 85°C, 100 hrs) was 2X lower than on unstressed cells and was correlated with a chemical change at the CdTe surface, with Cu₂Te transformed to CuTe after stress.

¹ B. E. McCandless and R. W. Birkmire, Proc. 29th IEEE PVSC, 491 (2000).

² S.-H. Wei, S. B. Zhang, A. Zunger, *J. Appl. Phys.* **87** (3), 1304 (2000).

³ J. Hiltner, J. Sites, *AIP Conf Proc.* **462**, 170-175 (1999).

⁴ S. Hegedus, B. McCandless, R. Birkmire, Proc 29th IEEE PVSC, 535 (2000).

Sincerely,

Robert W. Birkmire
Director

RWB/bj

Cc: Brian McCandless
Kevin Dobson
Steven Hegedus
Gerri Hobbs, UD Research Office
Paula Newton
Carolyn Lopez, NREL